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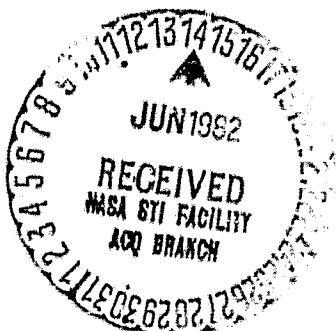
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ELECTRONIC LEVELS AND CHARGE DISTRIBUTION

NEAR THE INTERFACE OF NICKEL*



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SYNOPSIS

By means of a series of cluster calculations using both the multiple scattering $X\alpha$ and a new computational technique (designated SSO) which avoids the muffin-tin approximation, we have investigated the energy levels in clusters of nickel atoms and compared the results. The point group symmetry of the cluster has significant effect on the energy of levels nominally not occupied. This will influence the electron transfer process during chemisorption. The SSO technique permits us to treat, as a cluster, the approaching atom or molecule plus a small number of nickel atoms. Specifically, we have calculated that molecular levels become more negative in the O atom, as well as in a CO molecule, as the metal atoms are approached. Thus, electron transfer from the nickel and bond formation will be facilitated. This new type of result is of importance in understanding chemisorption and catalytic processes.

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The subject of chemisorption has long been a subject of scientific interest since the distinction between it and physical adsorption was made before 1930. Since this paper will be devoted to calculation of a chemical physical nature, it is well to cite some of the criteria by which chemisorption is recognized.¹⁾ Quoting from Trapnell²⁾, "a). Adsorption is localized and takes place through collision of gas molecules with vacant sites of the substrate. b). each site can accomodate one and only one adsorbed particle molecule and c). the energy of an adsorbed particle is [substantially] the same anywhere on the surface, and is independent of the presence or absence of nearby adsorbed molecules."

The experimental developments have been very significant and the migration of species has been demonstrated by Ehrlich³⁾, a number of measurements on the kinetics of activated adsorption have been made⁴⁾ and Gomer and his Colleagues⁵⁾ have observed surface structures directly. The disruption of surface layers as observed by Germer and MacRae⁶⁾ for the chemisorption of hydrogen on nickel is particularly significant since it stimulated many studies which showed that reconstitution apparently occurs in many surface systems.

In contrast, the theoretical analysis has not kept pace in this author's opinion.

Various hypotheses have been advanced to explain the relatively strong bond which is formed between the adsorbate and the substrate. These have perforce

largely dealt with phenomenological aspects of the adsorption process. It is worthwhile to summarize the various approaches taken before turning to the present method. Eley⁷⁾ calculated adsorption bond energies by taking the difference of the bond energy of D_{MH} (for metal-hydrogen bond) and D_{HH} (the dissociation energy of a H_2 molecule.) He also included the difference in the electronegativities χ proposed by Pauling⁸⁾. Eley included a dipole energy, again obtained from $(\chi_M - \chi_H)$. Even with a variety of approximations and improvements, the energies are not in good agreement with experiment. The difficult point is to adequately estimate the D_{MH} term when only a few "bonds" are broken.

Trapnell⁹⁾ has observed that the heats of adsorption for a variety of gases such as H_2 , O_2 , N_2 , CO , CO_2 , etc. generally decrease for the series of transition metals as one goes from Ti to Ni and Cu. This trend corresponds to a decrease in the number of available unoccupied d-levels. So, the d electrons participate in some significant way and many of the theoretical approaches to be discussed below have their greatest difficulties in dealing with such electrons. Further, the misleading statements exist in the literature which suggests that these electrons are very localized in transition metals and they cannot participate in bonding. Waber¹⁰⁾ has presented the radial distribution of d-like crystal orbitals (obtained by the Augmented Plane Wave Method) and it is clear that the d-electrons have appreciable probability of being found at the surface of a Wigner-Seitz sphere.

Pauling¹¹⁾ has introduced the idea of resonating covalent bonds (such as dsp) and this has brought the thinking of many scientists--despite the fact that they may not agree with all the details) to the point that the d-character of possible bonds are included in their thinking and explanations.

Another type of treatment assumes considerable electron transfer and the formation of M^+A^- bonds. Then the problem of chemisorption is reduced to making calculations of the Born-Mayer type. While such an approach has the merits of simplicity, it tends to oversimplify, to ignore image potentials (due to charge accumulation on the surface of a continuum.) In these attempts, the metal is not carefully included in the system. Bennett and Falicov¹²⁾ attempt a more careful analysis but in the end, resorted to treating tungsten as a free-electron metal.

A variety of quantum-mechanical approaches have been used. These started with Wall¹³⁾ and were more carefully studied by Higuchi and Eyring¹⁴⁾. They treat the surface complex as a diatomic molecule. The diagonal element of the Hamiltonian (which will be discussed below in terms of the present method) they write

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$$H_{11} = A_0 - I_e + 8/9 (e^2/r^*)$$

where A_0 is the electron affinity and I is the ionization potential. Here r^* is the radius giving the minimum. Again, they resort to substantial approximations and the interpretation in terms of partially ionic character of the bond formed in the complex, does not significantly modify the valuable ad hoc approach taken by Eley and Pauling.

Another popular type of treatment is to use the Valence Bond approach particularly in terms of the angular parts of atomic orbitals. Note that the potential field of the metal does not give rise to spherically symmetric potentials. Thus, the degeneracy of certain atomic levels is lifted as it is in crystal field theory and ligand field theory. Classical treatments of that type are by Goodenough¹⁵⁾ and Orgel¹⁶⁾. These authors deal with primarily atoms

(or ions) surrounded by a uniform or symmetrical arrangement of ions. Balkhausen¹⁷⁾ treats the more complex problem of electron clouds surrounding the ligands rather than point charges. A more detailed attempt to take account is the lower symmetry of the arrangement of substrate atoms (on various planes) which was recently published by Rao and Waber¹⁸⁾. Their specific assumption was that as far as an approaching atom was concerned, it experienced a non-uniform potential from the nearby substrate atoms as though they had a net unsatisfied charge in the vicinity of 0.1 of an electron.

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To this collection of quasi-chemical approaches, the important review by Schrieffer¹⁹⁾, should be added. to put the more physical aspects into proper perspective. This contains discussions to the work of Grimley²⁰⁾, Woyciechowski²¹⁾, Gadzuk²²⁾, News²³⁾ and Plummer and Rhodin²⁴⁾. Unfortunately the excellent recent work by Lange and Kohn^{25,26)} is not referenced. Space limitations cause us to bypass the details of such treatments but the interested reader is directed to these primary sources to amplify his understanding of recent quantum mechanical approaches. Schrieffer's review puts the various treatments into a framework where they can be judged against one another.

Several recent attempts have been made to elucidate the mechanism in quantitative form using molecular orbital approaches. Of this genre, the work by Messmer et al²⁷⁾ on the adsorption of various gases on layers of graphite could be cited as an example of one molecular orbital approach to surfaces. To avoid the calculation of certain integrals, he resorted to an approximation known as Complete Neglect of Differential Overlap (CNDO.) Another important recent development was the adaptation of the multiple scattering X α (MSX α) method of molecular calculation developed by Keith Johnson, John Slater and their collaborators²⁸⁻³⁰⁾. For clusters, this method characteristically relies on treating the potential around each atom site in a special way -- that is, inside each sphere of radius

of r_I the potential is substantially atomic (central field approximation.) However, in the region outside r_I the potential is spherically averaged at a constant value. This can be described as a "muffin-tin" potential since the radial regions centered at each of the I^{th} and J^{th} nuclei in a cluster may be in contact but do not overlap, i.e., $r_I + r_J \leq d_{IJ}$, where d_{IJ} is the interatomic distance. The values of r_I and r_J are generally chosen to be similar to the atomic (or ionic) radii given either by Slater³¹⁾, Waber and Cromer³²⁾ or Pauling³³⁾. A very recent development by Johnson et al³⁴⁾ and independently by Liberman³⁵⁾ is to permit the spherically averaged external regions to overlap so that d_{IJ} will be less than the sum of r_I and r_J . Danese and Conklin³⁶⁾ have been investigating this method.

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The present method retains most of the very desirable features of the (MSX) method of molecular calculation but further relaxes this condition of spherically smoothed potentials. It has evolved from a number of studies which were carried out by Ellis and Painter³⁷⁾ using the Discrete Variational Method (DVM) to calculate observable quantities of molecular clusters.

In DVM one presumes that they can obtain a very good representation of the values of the collection of important interatomic integrals by evaluating their integrands at a discrete set of points. For this purpose, Ellis and his coworkers^{37,38)} used a basis set of Gaussians and Slater-type orbitals in the regions outside r_I and r_J but solved the atomic Hamiltonian inside the individual spherical regions surrounding the I^{th} and J^{th} ion cores. To emphasize this difference in the two approaches, one notes that Johnson and coworkers used spherical waves (similar to those used in the Korringa-Kohn-Rostacker⁽³⁹⁾ (KKR) method for band structure calculations) in the extraspherical (or interatomic) region. Painter⁴⁰⁾ investigated the use of a linear combination of KKR orbitals in connection with

At essentially the same time, Averill and Ellis⁴¹⁾ and Painter and M. Stock⁴²⁾ recently proposed using a linear combination of atomic orbitals. Because the orbitals for excited states tend to be diffuse, they imposed a high potential barrier at a reasonably large distance so as to localize the Rydberg orbitals but not disturb the minimal basis set of bound atomic orbitals. For this reason they labelled their method Single Site Orbital (SSO). Because of Close collaboration over the years, these two treatments are very similar.

It should be pointed out that the (MSX α) method the cluster of atoms is confined by a larger sphere. Thus it does not readily lend itself to treatment of an atom or molecule approaching a cluster. In contrast, restriction is lifted since the SSO was specifically designed to treat the angular variation of the molecular potential in the region between and outside the spheres, while keeping the excited orbitals in the basis set "well behaved."

Method of Computation

The basic problem in all such atomic and molecular structure problems is to obtain eigen-values and eigenfunctions for a one-electron Hamiltonian \mathcal{H} where $V(\mathbf{r})$ represents some approximation to the potential an electron experiences in the molecule. Such an eigenfunction may be written as

$$\chi_i(\mathbf{r}) = \sum_j \chi_j(\mathbf{r}) c_{ij} \quad (1)$$

where the functions $\chi_i(\mathbf{r})$ are symmetrized linear combinations of single site orbitals

$$\chi_i(\mathbf{r}) = \sum_{n,l,m} W_{nm}^{i,l} U_{nl}(r_U) Y_{lm}(\hat{r}_U) \quad (2)$$

where the $U_{nl}(r)$ and Y_{lm} are the radial and angular functions centered at the U^{th} ion core and n , l and m are the appropriate quantum numbers. There is not sufficient space to show how the symmetrization coefficients can be obtained by group theory--it is sufficient to indicate that j identifies a particular basis function for the irreducible representation. The radius r_U is the distance between the U^{th} nucleus and the radius vector \mathbf{r} .

The matrix elements which need to be calculated are

$$\mathcal{H}_{ij} = \langle \chi_i | \mathcal{H} | \chi_j \rangle \quad (3)$$

$$S_{ij} = \langle \chi_i | \chi_j \rangle \quad (4)$$

The distinguishing feature of the Discrete Variational Method in contrast to the Rayleigh-Ritz method, is that such matrix elements are evaluated as

$$H_{ij} = \sum_{k=1}^N W(r_k) \psi_i(r_k) \left[-\nabla^2 + U(r_k) \right] \psi_j(r_k)$$

where the three components of r_k (in real space) are determined randomly. Here $W(r_k)$ is an appropriate weighting factor applied at each of the N points.

The spacial density of points need not be uniform. In fact, Averill and Ellis use a distribution which is similar to the two parameter Fermi distribution of protons in a nucleus, that is

$$d_U(r) = \frac{A_U}{4 \pi r_U^2 \left\{ 1 + \exp \left[\beta_U (r_U - R_U^0) \right] \right\}} \quad (6)$$

where A_U is a normalization constant. The probability of a point occurring in a spherical shell of radius r_U is $A_U/2$ when $r_U = R_U^0$. The distribution is essentially uniform at the value A_U until r_U is close to R_U^0 and then approaches zero rapidly with a "decay" constant or "e-folding" distance of β_U^{-1} .

Since these distributions of sample points are centered about each ion core, Averill and Ellis use a linear combination of these

$$D(r) = \sum_U t_U d_U(r) \quad (7)$$

where t_U is an adjustable sampling factor for the U^{th} atom. They chose $\beta_U = 1$ and R_U^0 equal to the atomic radius. The total number N of points at which

the integrands are sampled influence the accuracy of finding eigenvalues.

To obtain the Single Set Orbitals, they chose

$$V_{sso}^V(r) = \begin{cases} V_a^V(r) - V_s^V & r \leq R_V^s \\ 0 & r > R_V^s \end{cases} \quad (8)$$

and solved the equation

$$\nabla^2 \psi_{lmn}^V = [V_{sso}^V(r) - E_{nl}^V] \psi_{lmn}^V(r) \quad (9)$$

for the atomic like eigenfunctions.

The basic set of bound atomic orbitals is minimal, but too small to include interatomic interactions. However, reasonable Rydberg states can be found by a judicious choice of the well depth V_s^V and the well radius R_V^s without affecting the bound orbitals appreciably.

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The results obtained to-date are of two types: (a) the energy levels in small clusters of nickel atoms were found by a variety of different methods and for two spatial conformations D_{4h} and T_d --these results are compared below--and (b) the shift in the electronic levels of an oxygen atom and of a CO molecule as it approaches such a cluster of Ni atoms. The latter result is of significance for chemisorption and for the reactions between an atom and an interface.

In Fig. 1, the eigenvalues obtained after the first iteration are compared for two different arrangements of five nickel atoms. The free atom values are for 3d and 4s, assuming an initial configuration of $3d^8 4s^2$. Because of the higher symmetry in the T_d cluster, there are fewer (but more degenerate) molecular levels than for D_{4h} . This is readily seen for the hybrid excited levels. The same trend is true for the more deeply buried 'core' levels as shown in Fig. 2.

A very important variation of the valence eigenvalues with method of calculation is shown in Fig. 3. In the first group, are the results for the MSX2 "Muscatel" program developed by Johnson et al. The second group is for a modification of the present method (DVM-SSO) in which spherical averaging of the interatomic potential has been imposed to facilitate comparison with the MSX2 results. The effect of relaxing this arbitrary condition in SSO calculations is also shown. The shifts in the levels near -0.7 Ry are interesting. These levels were obtained with N=500 sampling points. In the first three panels of Fig. 3b, the molecular levels obtained for 1000, 2000 and 4000 sampling points in the Diophantine integration scheme of DVM. It is surprising that the principal shifts occur in BlG level at the top of the drawing as well as for the four hybridized levels below -0.7 Ry. An additional set of results obtained for an increased interatomic separation in the D_{4h} conformation are shown in the last

panel of Fig. 3b. The low lying levels were not plotted for valence electrons.

The graphs showing similar effects on levels derived from 3p and 3s states have been plotted but they are not included.

Since no efforts have been made to carry out the DVM-SSO results towards self-consistency, it is important to investigate the effect of the successive iteration on the Muscatel eigenvalues. This is presented in Fig. 4. While some shifts do occur with the approach towards self-consistency, the excited levels seem insensitive. The major changes occur in the ordering of the strongly interacting levels derived from the 3d atomic state. Large shifts are also apparent. But after 15 cycles, the levels do not vary greatly from those obtained after the first iteration. This data is of interest to both a practitioner in the field and to experimentalists wishing to interpret spectra, but has little influence on the general information to be gleaned by comparing the first-pass Td and D_{4h} calculations presented in earlier figures.

These results on small clusters may be compared with the results soon to be reported by Diamond, Messmer, Knudson and Johnson⁴³⁾ whom studied clusters containing 13 or more atoms of nickel and copper. There, more states will be found because of the difference in coordination numbers for atoms in the suboctahedral and icosahedral clusters.

The two portions of Fig. 5 are composite drawings. On the left-hand side, the density of curve for face centered cubic nickel which was computed by Snow and Waber⁴⁴⁾ assuming a Dirac-Slater SCF atomic calculation with $3d^9 4s^1$ configuration as input. The other parameter was Slater's exchange coefficient α_s , which was used as unity in accord with Slater's original α derivation⁴⁵⁾.

Had a lower value approaching two-thirds been used, the d-bands would have appeared at more positive values on this energy scale. It is important to point out that the vacuum level is a natural one for comparing a variety of calculations. That is, the potentials for either a cluster calculation or a band calculation depend on superimposition SCF atomic potentials. For these, the zero corresponds to an electron removed to infinity. Following superposition, this level is not modified. The χ procedure of summing the individual SCF charge densities before taking the cube root does not alter this potential scale since the net charge density vanishes at $+\infty$ for a semi-infinite solid. Snow and Waber⁴⁴⁾ based all their band calculations on this scale rather than comparing the $E(k)$ values with the muffin-tin potential (taken as zero.)

In the right-hand side of Fig. 5a, the variation of the molecular orbitals in a cluster of oxygen approaching a C_{4v} cluster of nine nickel atoms* are shown. The separation corresponds to the distance from the oxygen atom to the center of the plane passing through nickel nuclei. Both the doubly degenerate E and non-degenerate A_1 level falls rapidly as the potentials from the nickel atoms increase the potential seen at the oxygen nucleus. This leads to more negative eigenvalues. Transfer of an electron from the nickel towards the oxygen and bond formation would be anticipated. So far, the perturbation of the nickel atoms in the cluster caused by the oxygen have not been extracted from the calculated data.

Comparing the levels with only five nickel atoms in Fig. 1 with the right-hand side of Fig. 5a, the possibility of transfer is even stronger since

*Averill, Adachi & Ellis⁴⁶⁾ assumed free atom configuration of $3d^8 4s^2$ for nickel in these clusters.

these Ni-only values lie at more positive values. The value of α_g that Averill et al⁴⁶⁾ used was 0.70843 and the separation between Ni atoms was 4.709 Bohr.

The work function for pure nickel varies between 4.07 and 5.1 eV according to Hagstrom⁴⁷⁾ but one has to take into account the transition state effects associated with promotion of an electron into the continuum and creation of a hole in the d-bands. It would seem not worthwhile in the preliminary stage before achieving self-consistency in these SSO calculations to argue about exact locations. If indeed the Fermi level in nickel metal is more positive, the importance of this work to chemisorption remains true a fortiori.

A similar situation obtained Fig. 5b--the right-hand side pertains to the shift in the molecular orbitals of carbon monoxide as it approaches a C_{4v} cluster of 5 nickel atoms. This graph has been shifted upward by 0.2 Ry to show the lower lying states in CO; however, the vacuum level is no longer directly indicated. As above, the presence of the nickel atoms gives rise to an increasingly negative potential experienced more by the C atom than the O atom. Levels shift sufficiently to facilitate electron transfer and bond formation.

These results appear to be the first time that it has been shown that the metal is directly influencing either atomic or molecular levels as species approach a surface. Gadzuk²²⁾ and Schrieffer¹⁹⁾ discuss such transfer processes and resonance broadening in terms of the free atom levels (plus ionization potentials and electron affinities) in the approaching species. The present results show that the situation is more complicated than indicated in previous treatments.

The use of the density of states is pertinent for chemisorption since relatively large specimens and particles have been used experimentally. The work on small clusters is pertinent to general problems in catalysis since

small aggregates of dimensions of 10 to 50 Å are dispersed on a support such as amorphous silica or alumina. The "Fermi level," below which the states are not occupied in the nickel clusters, is E_u for D_{4h} and T_2 for T_d , namely, in the range of 0.3 to 0.4 Ry. Note that this level is reasonably consistent with the experimental value of 5eV for the work function. The work by Johnson and Messmer⁴⁸⁾ on a single nickel cation surrounded by six oxygen anion O^{--} is related to the results in Fig. 5a. They obtain a similar "Fermi level."

The results in Fig. 5b should be compared with the results which Messmer, Yong and Johnson⁴⁹⁾ are currently obtaining for CO and ethylene on small metallic clusters. Doubtless similar trends will be found.

Note that the surface field analysis by Rao and Waber⁴⁷⁾ has indicated some of the trends found in the present more detailed molecular analysis. In Fig. 3a of their paper, for a p^4 configuration such as for the oxygen atom, the p_x and p_y levels were degenerate and are energetically above p_z . The relative shifts of the two levels was small (ca. 0.07, eV) but their positions "flipped" as the atom approached nearer the plane of nickel atoms, than h/a of 0.6. In reference to their Fig. 10, the barycenter E_{avg} of these two levels was strongly shifted and depends on the evaluation of the Y_0^0 spherical harmonic which is not usually tabulated in crystal field calculations. The present Fig. 5a clearly shows the predicted shifts. The doubly degenerate E levels lie above A_1 when the oxygen atom is sufficiently far away but occurs below their barycenter when the oxygen separation is less than three Bohr units. The shift in the barycenter is an order of magnitude larger than the $E \rightarrow A_1$ separation.

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Fig. 1. The comparison of the molecular eigenvalues for clusters of five nickel atoms arranged with T_d and D_{4h} symmetry. Result of the first iteration with the MSX or "Muscatel" computer program.

Fig. 2. Similar Comparison of the Hybrid States derived from more tightly bound electrons.

Fig. 3a. Comparison of the results for states associated with 3d electrons obtained with different computing techniques. The second column is for DVM-SSO calculations with a spherically averaged interatomic potential so that they can be compared with the Muscatel values. The third column illustrated the effect of relaxing this smoothing procedure. Both DVM-SSO calculations were done with $N=500$.

Fig. 3b. The gradual shifts in the levels for the D_{4h} cluster of five nickel atoms with increased number N of sampling point. The last column illustrates the effect of increasing the interatomic distance from 4.709 to 6.5 Bohr units.

Fig. 4. Illustration of the shift in individual energies of molecular states with successive iterations towards self-consistency.

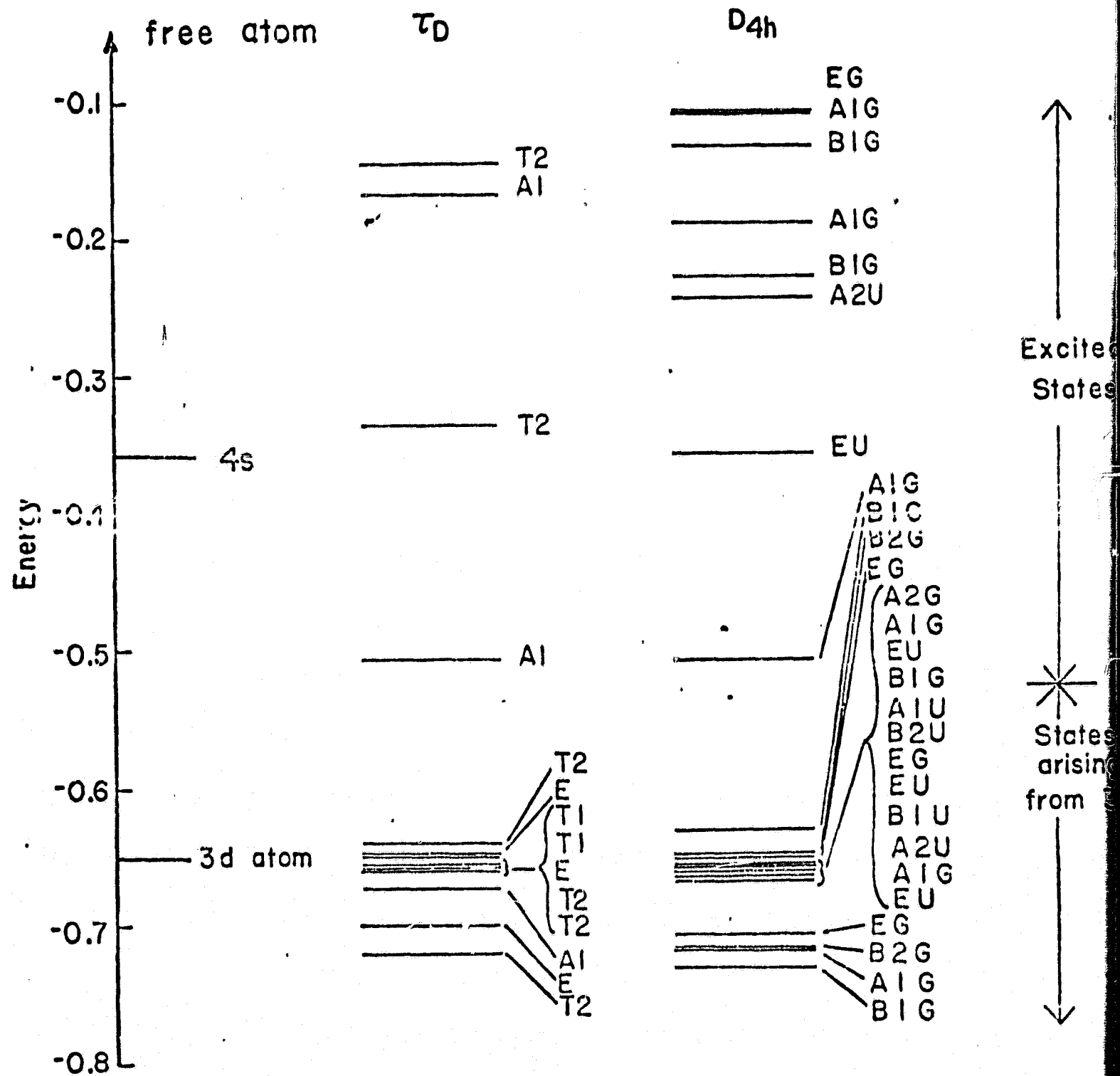
Fig. 5a. Composite graph showing on the left, the density of states curve derived by Waber and Snow⁴⁷⁾, assuming face center cubic nickel and a Slater's exchange coefficient of $\alpha_s=1$. The Fermi level appears to be lower than the observed work function of about 0.35 Ry. On the right, the shift in the molecular eigenvalues of an oxygen atom as it approaches a

cluster of 9 nickel atoms.

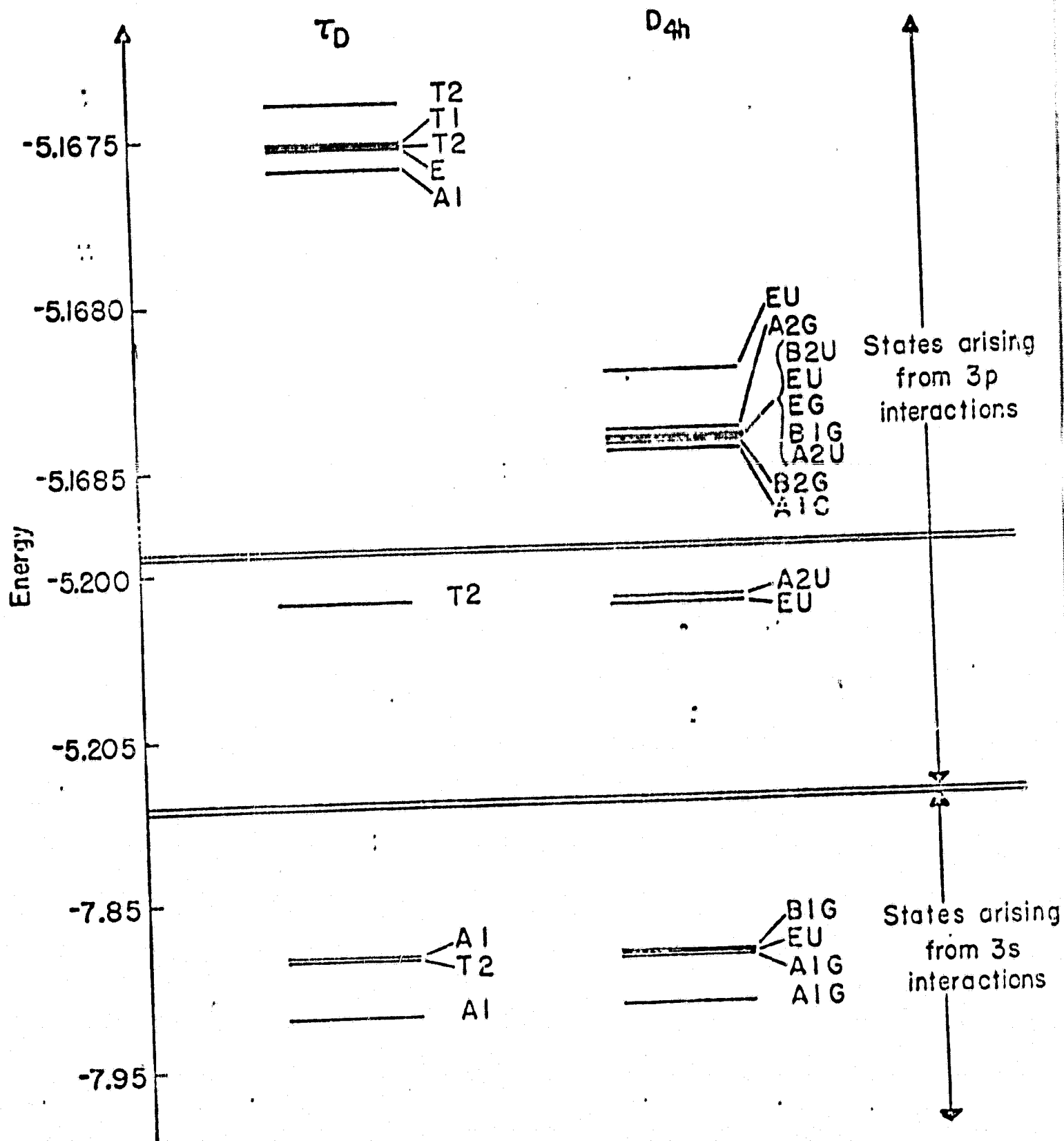
Fig. 5b. A similar comparison showing the downward drift of molecular states in carbon monoxide as it approaches a cluster of 5 nickel atoms.

This has been shifted upward by 0.2 Ry, compared to Fig. 5a, to show additional CO states.

Starting Potentials



Starting Potentials

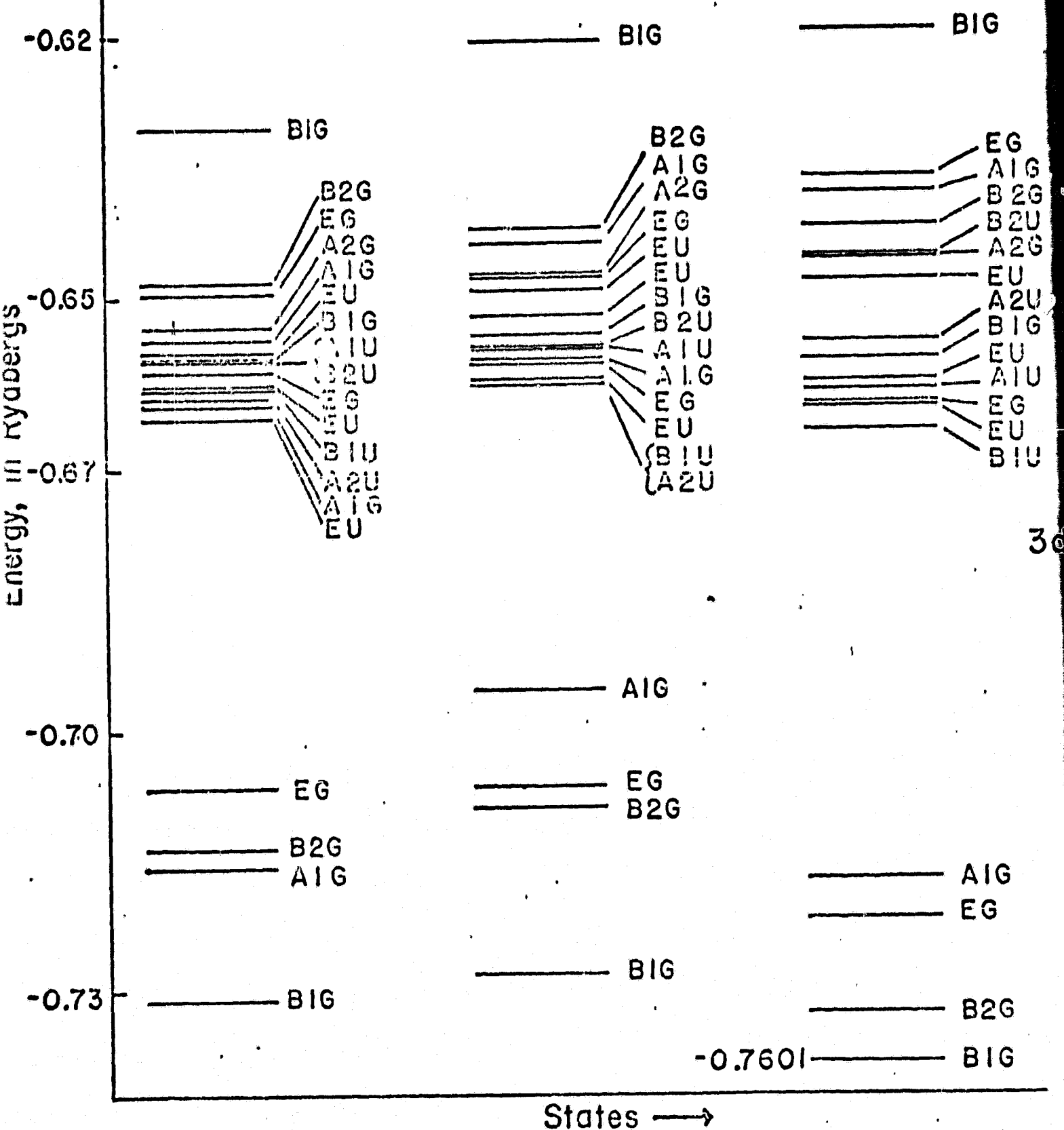


MUSCATEL

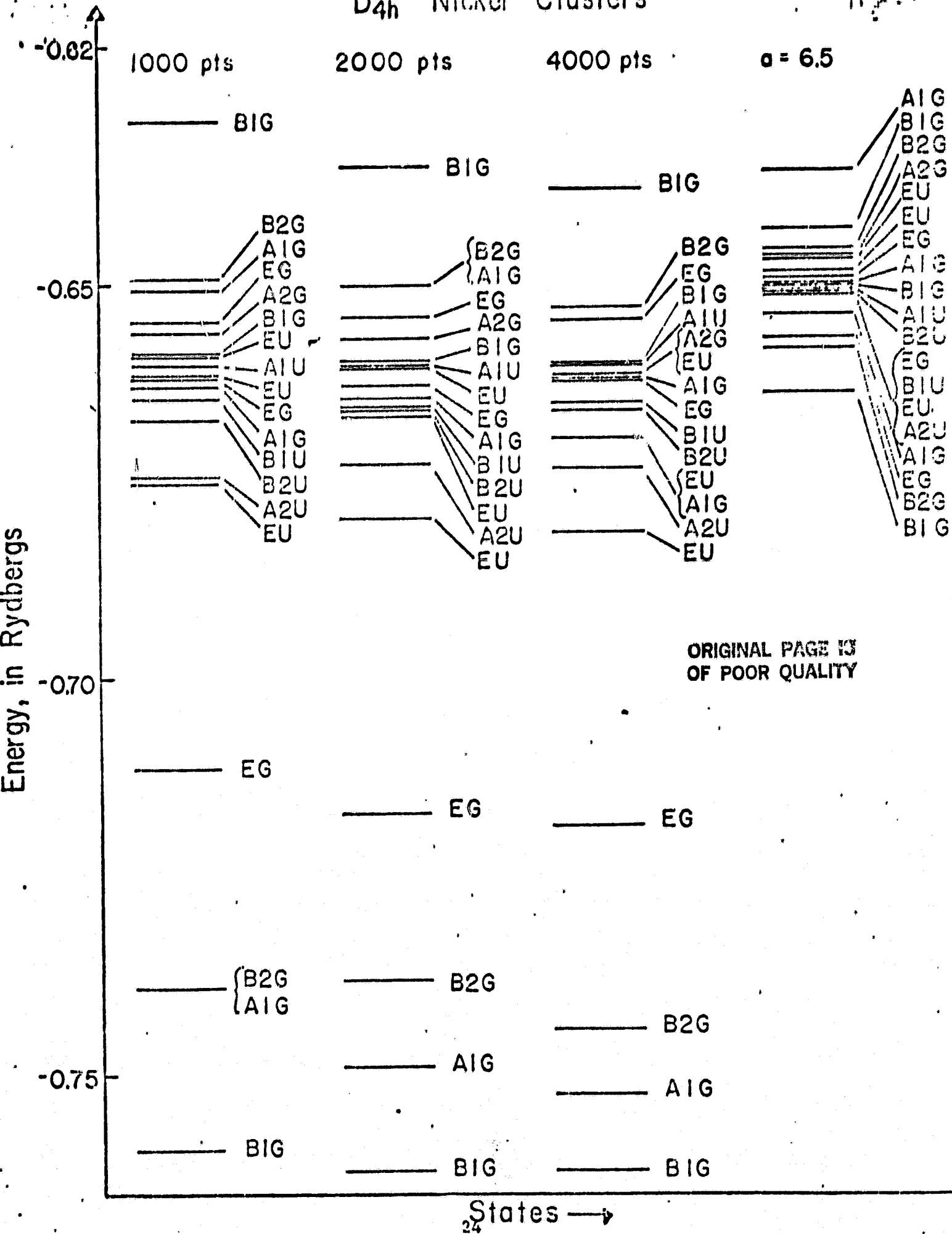
MUFFIN TIN

NON-MUFFIN TIN

-0.5884 ——— AIG

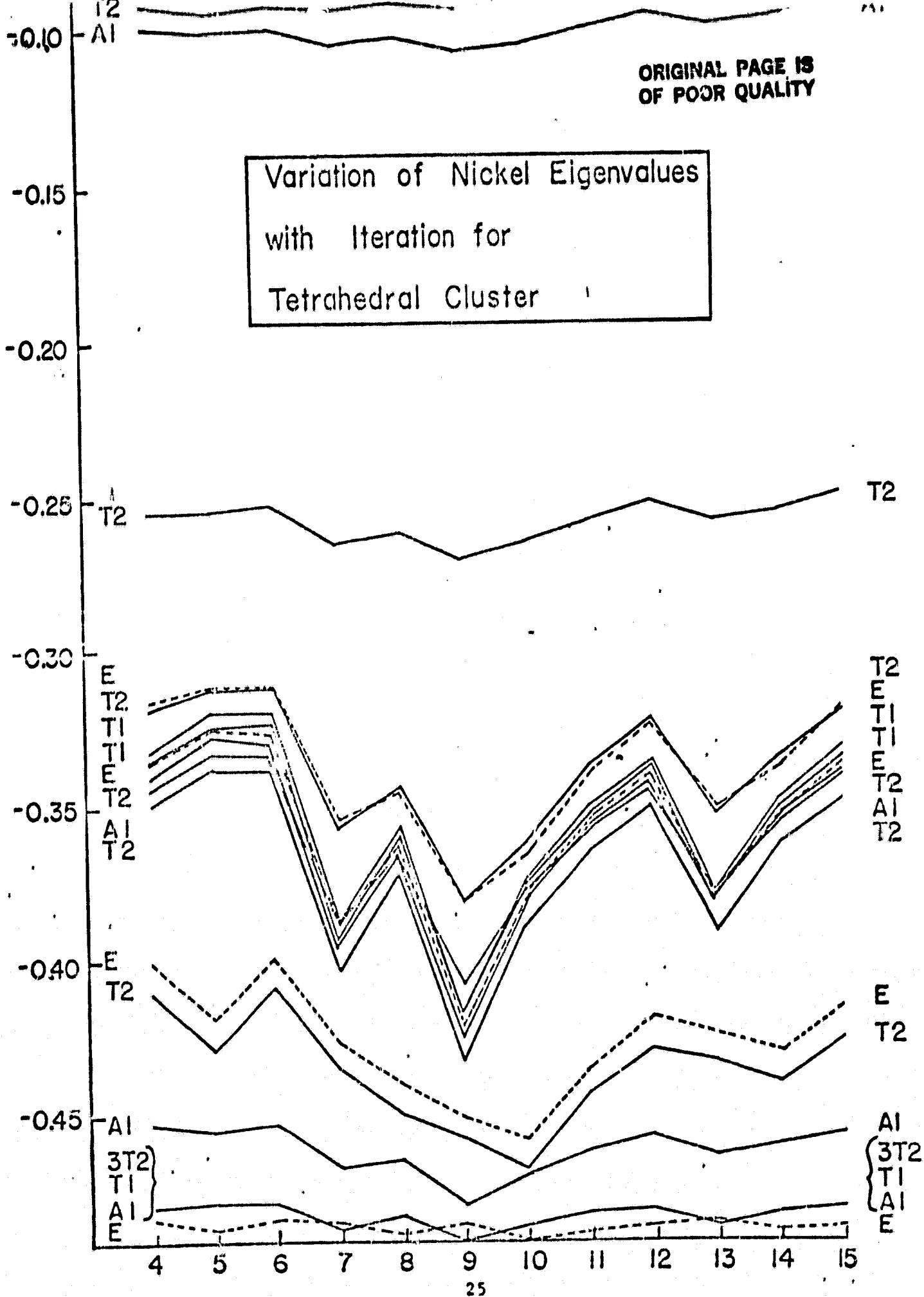
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D_{4h} Nickel Clusters



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Variation of Nickel Eigenvalues
with Iteration for
Tetrahedral Cluster



Vacuum Level

F.C.C. Nickel Metal

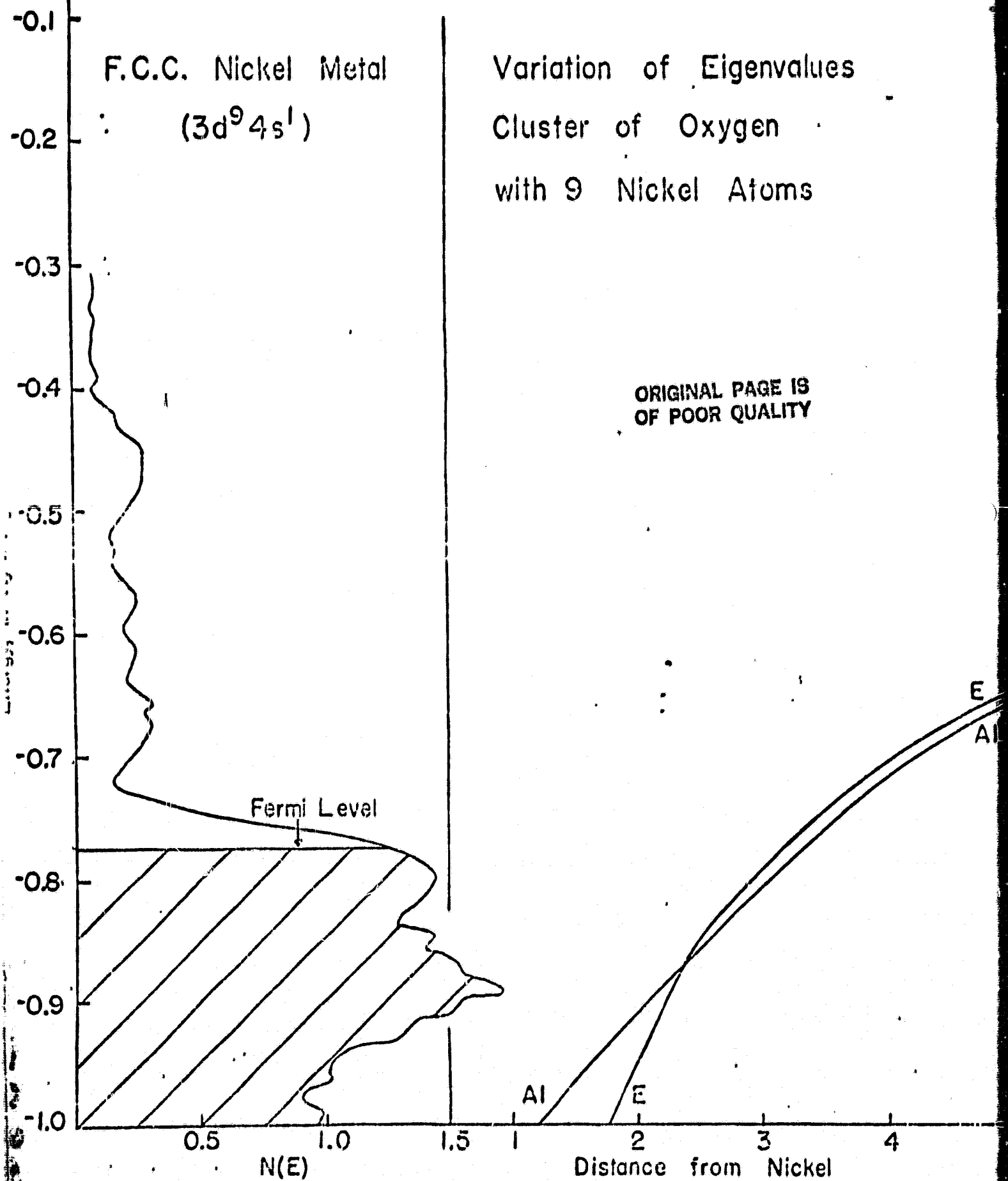
($3d^9 4s^1$)

Variation of Eigenvalues

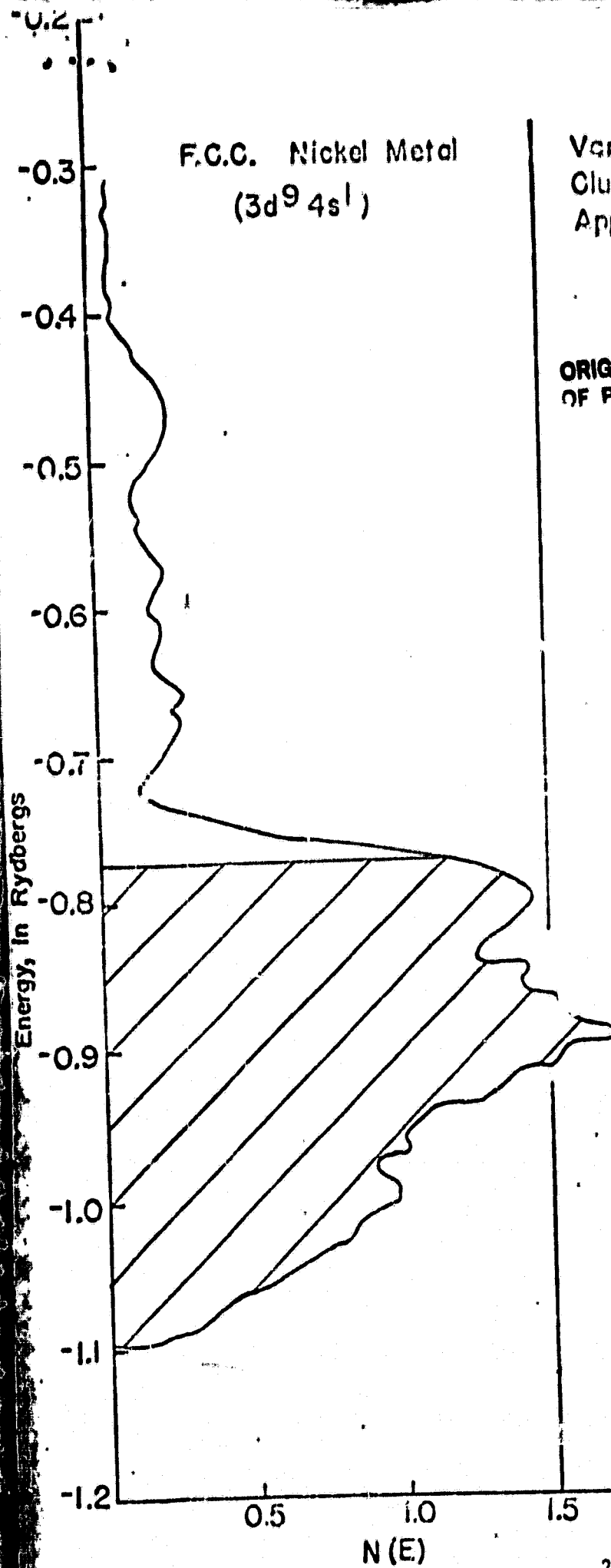
Cluster of Oxygen

with 9 Nickel Atoms

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F.C.C. Nickel Metal
($3d^9 4s^1$)



Variation of Eigenvalues
Cluster of Carbon Monoxide
Approaching 5 Nickel Atoms

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